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DETERMINATION OF THE RELATIVE AMOUNT OF FLUORINE
IN URANIUM OXYFLUORIDE PARTICLES
USING SECONDARY ION MASS SPECTROMETRY AND OPTICAL SPECTROSCOPY

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ABSTRACT

Both nuclear forensics and environmental sampling depend upon laboratory analysis of nuclear material that has often been exposed to the environment after it has been produced. It is therefore important to understand how those environmental conditions might have changed the chemical composition of the material over time, particularly for chemically sensitive compounds.
In the specific case of uranium enrichment facilities, uranium-bearing particles stem from small releases of uranium hexafluoride, a highly reactive gas that hydrolyzes upon contact with moisture from the air to form uranium oxyfluoride (UO_2F_2) particles. The uranium isotopic composition of those particles is used by the International Atomic Energy Agency (IAEA) to verify whether a facility is compliant with its declarations. The present study, however, aims to demonstrate how knowledge of time-dependent changes in chemical composition, particle morphology and molecular structure can contribute to an even more reliable interpretation of the analytical results.

We prepared a set of uranium oxyfluoride particles at the Institute for Reference Materials and Measurements (IRMM, European Commission, Belgium) and followed changes in their composition, morphology and structure with time to see if we could use these properties to place boundaries on the particle exposure time in the environment. Because the rate of change is affected by exposure to UV-light, humidity levels and elevated temperatures, the samples were subjected to varying conditions of those three parameters.
The NanoSIMS at LLNL was found to be the optimal tool to measure the relative amount of fluorine in individual uranium oxyfluoride particles. At PNNL, cryogenic laser-induced time-resolved U(VI) fluorescence microspectroscopy (CLIFS) was used to monitor changes in the molecular structure.

INTRODUCTION

Gaseous uranium hexafluoride (UF_6) is used for the enrichment of uranium and is known to be a very reactive and volatile gas. UF_6 reacts vigorously with water and is therefore handled in leak-tight containers and installations to prevent it from reacting with the water vapor in the air. Despite these precautions, small releases of UF_6 do occur during normal plant operation. When released into the atmosphere, UF_6 is rapidly hydrolyzed to form hydrogen fluoride (HF) and uranium oxyfluoride particles [1]. The particles that are formed this way are deposited on various surfaces within and

outside the facility. Despite their small size, they typically contain a vast amount of information on both the present and past activities at the enrichment plant. This is why safeguards organizations such as the International Atomic Energy Agency (IAEA) collect these particles to detect the presence of undeclared nuclear activities. This technique is generally referred to as 'Environmental Sampling' and applies highly selective and sensitive instrumentation to determine the uranium isotopic composition of individual particles [2].

What makes UO_2F_2 particles particularly interesting is that they lose fluorine over time and through the exposure to certain environmental conditions [3,4]. The measurement of the residual amount of fluorine in these particles therefore has the potential of placing boundaries on the exposure time in the environment. For our experiments, we prepared a set of UO_2F_2 particle samples at the Institute for Reference Materials and Measurements (IRMM, Geel, Belgium), expressly for the purpose of this study, and compared the fluorine content and molecular structure at different stages in the ageing process. The particles were analyzed using secondary ion mass spectrometry with nanometer-scale spatial resolution (NanoSIMS) and cryogenic laser-induced fluorescence spectroscopy (CLIFS).

EXPERIMENTAL

Uranium oxyfluoride particle samples
The uranium oxyfluoride particles used for this project were prepared at the IRMM, expressly for the purpose of these experiments. The aerosol deposition chamber at the IRMM was designed to produce uranium oxyfluoride particles for the development of reference materials for safeguards applications [5]. UF_6 gas is released in the chamber in an atmosphere with controlled temperature and humidity. Upon release, this UF_6 gas reacts with the atmospheric moisture forming UO_2F_2 particles and HF:

$$UF_6 + 2H_2O \rightarrow UO_2F_2 + 4HF$$
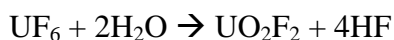
The UO_2F_2 particles formed in the aerosol deposition chamber were deposited on 9.525 mm diameter graphite planchets, 12.7 mm sapphire discs and zinc selenide substrates through gravitational settling. Slightly depleted UF_6 ($^{235}U = 0.704$ %) was used for all particle samples. The UF_6 was released in an atmosphere at room temperature with a relative humidity of around 60 %. These high humidity conditions typically result in spherical particles of around 1 micron in size [5].

The particle samples were shipped to the Lawrence Livermore National Laboratory (LLNL) in containers filled with argon gas to minimize the loss of fluorine during shipment. Upon arrival at LLNL, they were divided among 4 environmental chambers stored at different temperature, humidity and lighting conditions (Table 1). Glove-box type chambers (Electro-Tech Systems) were used for particle ageing in a dry atmosphere, while high humidity conditions were simulated in the two ThermoForma chambers.

Chamber type	ETS1	ETS2	ThermoForma1	ThermoForma2
Temperature	24 ± 1 °C	40 ± 2 °C	25.5 ± 0.3 °C	40.6 ± 0.1 °C
Humidity	< 15 %	< 15 %	76 ± 0.4 %	77 ± 0.4 %
Lighting	Daylight simulated/Dark	Diffuse lighting/Dark	Diffuse lighting	Diffuse lighting

Table 1. Temperature, humidity and lighting conditions of the four environmental chambers at LLNL for the storage of the UO_2F_2 particle samples

Scanning electron microscopy with energy-dispersive X-ray capability (SEM-EDX)
To verify the particle morphology after SIMS analysis, a field emission JEOL JSM-7401 SEM was used at LLNL. This microscope has a spatial resolution of 3 nm at 1 kV and is equipped with an Oxford INCA Si(Li) detector with an energy resolution of 137 eV at 5.9 keV. Measurements were typically carried out using a 10 kV accelerating voltage to be able to detect both the fluorine K_α-line (0.677 keV) and U M_α-line (3.16 keV).

Secondary ion mass spectrometry (SIMS)
The Cameca NanoSIMS 50 was used to assess the level of fluorine in UO_2F_2 particles. The combined ultra-high sensitivity and spatial resolution of this ion microprobe allowed for the analysis of individual particles both elementally and isotopically on the 50-100 nm scale (compared to the micrometer scale for conventional SIMS instruments). The measurements reported in this work were carried out using 16 keV primary oxygen (O^-) beam at a current of approximately 100 pA. Oxygen primary ion bombardment enhances the production of positive secondary ions, such as U^+. Fluorine is preferably detected as a negative secondary ion, however, the ion yield for F^+ was found to be sufficient under these measurement conditions.

Cryogenic laser-induced fluorescence spectroscopy (CLIFS)
The apparatus for fluorescence spectroscopic and lifetime measurements at liquid He-temperature (6 ± 1 K) has been described elsewhere in detail [6,7]. Sample excitation was achieved by 415 nm light from a MOPO-730 pulsed laser incident at right angle. After passing a 460 nm dichroic long-pass filter, the emitted light was dispersed by Acton SpectroPro 300i double monochromator spectrograph with a slit size of 100 μm and detected by a Roper Scientific intensified, time-gating CCD camera. Wavelengths were calibrated using a Spectra Physics model 6033 Xenon lamp. The spectrometer offered a spectral resolution of ~ 2 nm (FWHM) and the time-gated CCD camera provided a risetime of ~ 5 ns, and a variable time delay with a minimal step of one nanosecond. The data acquisition was automated by WinSpec data acquisition software and analyzed using the commercial software package IGOR.

RESULTS

At LLNL, the NanoSIMS 50 was used to determine the relative amount of fluorine in individual uranium oxyfluoride particles. Although this technique is highly sensitive, it was assumed that, under the exposure conditions listed in Table 1, it would take at least several weeks before the particles have lost a detectable amount of fluorine. The majority of the samples are therefore currently still being stored in the environmental chambers. A total of eight particle samples have already been analyzed however: six samples were taken out of the different environmental chambers after 7 weeks of storage, while the other two were kept in an inert atmosphere for 2-3 weeks until they were analyzed. The NanoSIMS measurements on these latter two samples provided the reference value for the initial amount of fluorine in freshly-prepared uranium oxyfluoride particles. No additional sample preparation was performed on any of the samples.

The following mass table was set up for the NanoSIMS measurements: $^{12}C^+$, $^{16}O^+$, $^{19}F^+$, $^{238}U^+$, $^{238}U^{16}O^+$, $^{238}U^{19}F^+$, $^{238}U^{16}O_2^+$. Because of the large mass difference between $^{12}C^+$, $^{16}O^+$, $^{19}F^+$ and the uranium compounds (m/z=238-270), the magnetic field setting needed to be changed during the analysis (peak jumping). The different ion species were collected in ion imaging mode, by rastering a highly-focused primary beam over a 7 μm x 7 μm area, centered on a particle or particle agglomerate. Variations in the ion intensities with sputtering were monitored by collecting ion images while cycling the magnet through the masses of interest (depth profiling). The analysis was stopped after the fluorine ion count rate was reduced to background. Between 3 and 6 areas were analyzed per sample. For data processing, custom software (L'Image, PXT PSearch) was used.

A typical depth profile obtained via NanoSIMS is shown in Figure 1. This sample was stored in dry air at 24 °C and exposed to simulated natural daylight. Even though the secondary ion intensities were transient and sputtering equilibrium was not reached, the depth profiles showed similar trends for the different particle samples. The C^+ count rate produced by the graphite substrate, and the O^+ count rate were stable throughout the analysis and were omitted from this plot for reasons of clarity. The UO^+ ions were the most abundant at the start of each measurement, with a typical count rate of around ten thousand counts per second. The fluorine count rate started off at around 500 cps, reaching its maximum in the first few cycles, after which it rapidly decreased to background levels. The UF^+ ions generally tracked the F^+ ions, although the sharp maximum that was seen for fluorine was not observed for UF^+. The analysis was stopped after approximately 30 minutes of sputtering, when the fluorine ion intensity was reduced to a few counts per second. The uranium counts at that point were still in the range of 10^3-10^4 cps, and this implies we did not completely sputter through the particle. Extrapolation of the U^+ ion intensity indicated that about 80 % of the particle volume was sputtered in this time. The EDX spectrum of a UO_2F_2 particle and the secondary electron image of an eroded particle after SIMS analysis are shown in Figure 2.
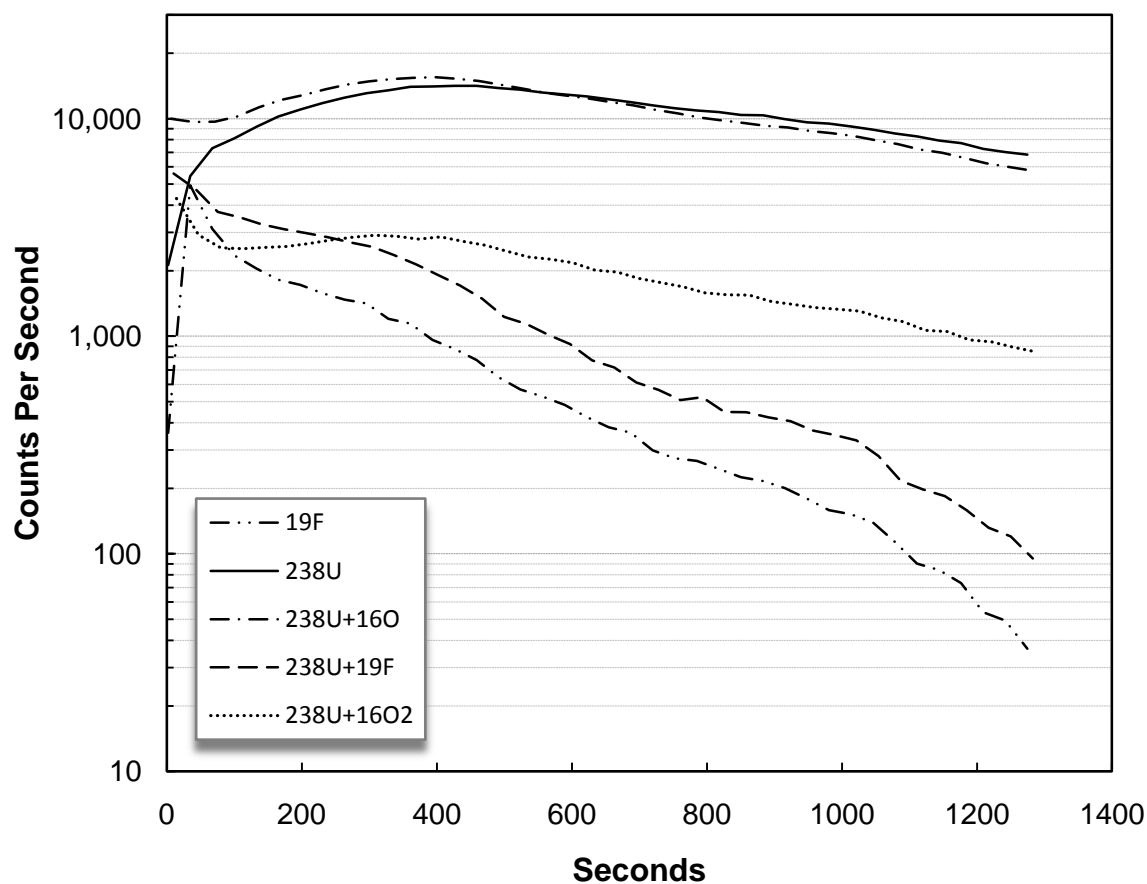
**Fig. 1.** Depth profile obtained by the Cameca IMS NanoSIMS 50 by sputtering a UO_2F_2 particle in a 7 μm x 7 μm raster. The fluorine signal increased rapidly after the start of the analysis, but was reduced to background after 1300 s of sputtering. The U^+ intensity was still at around 7000 cps at the end of the analysis, which suggested we did not completely sputter through the particle.
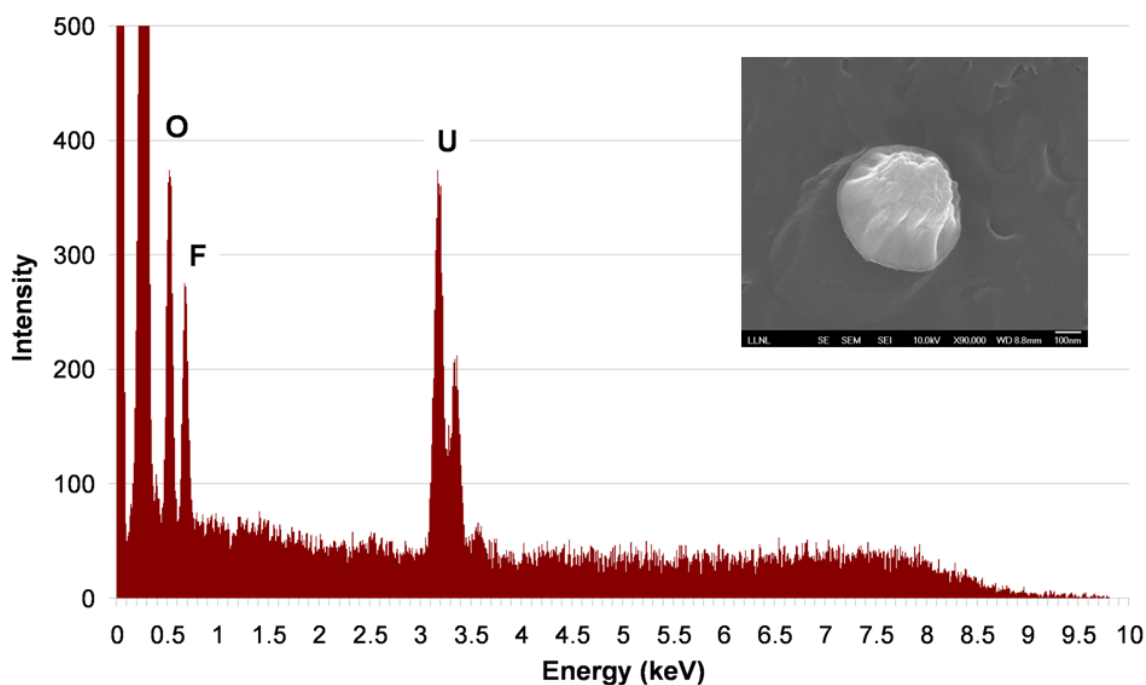
Fig. 2. SEM-EDX spectrum of a UO_2F_2 particle showing the U Mα lines, as well as the O and F Kα lines. The peak at 0.277 keV is produced by the graphite substrate. The secondary electron image on the right shows a UO_2F_2 particle with clear signs of erosion from sputtering with a primary ion beam.

In order to quantify the relative amount of fluorine for the various aged and freshly-prepared particle samples, the intensity of the fluorine ions was ratioed to the intensity of an ion characteristic of the uranium oxide matrix. The F^+/U^+ ratio was calculated from the total counts for F and U over the entire 7 μm x 7 μm raster, and the average values for the different samples were plotted in Figure 3.
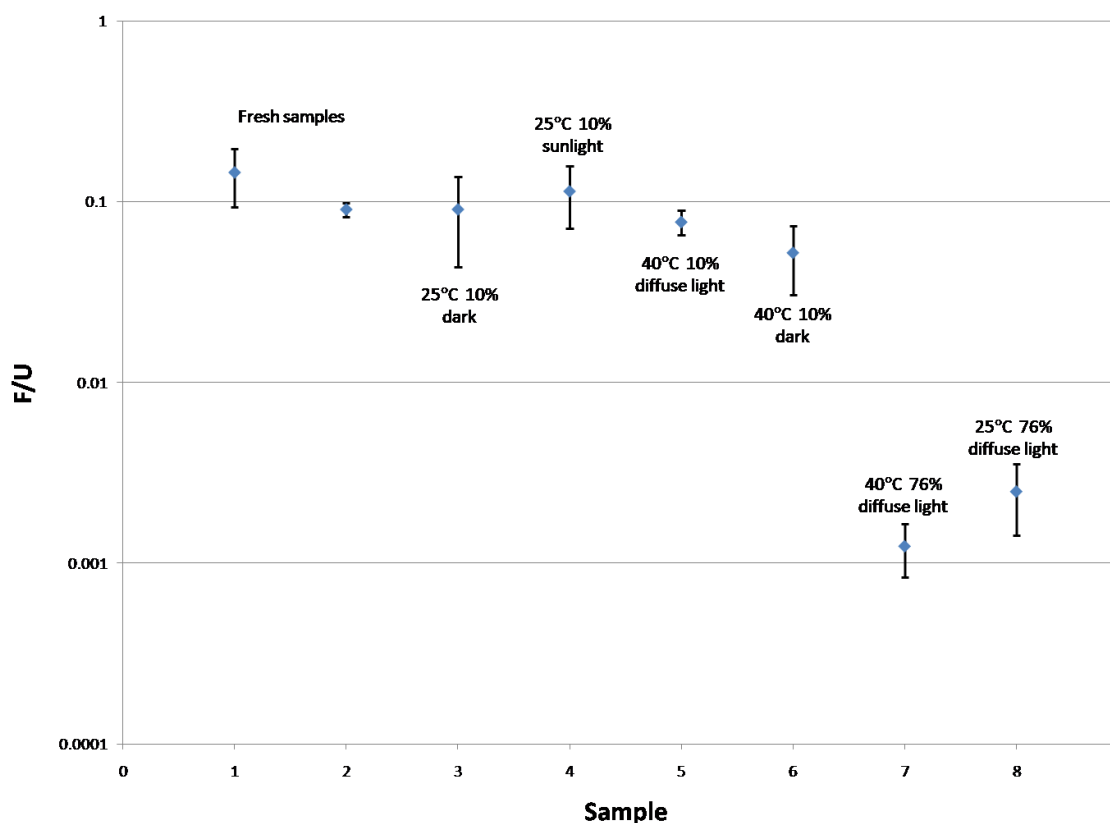
Fig. 3. NanoSIMS F^+/U^+ ratios from particle samples stored in different environmental conditions. High humidity storage led to a significant decrease in the relative amount of fluorine.

The error bars represent the standard error of the mean. The F^+/U^+ ratios for the freshly-prepared particle samples (1-2) was calculated at 0.14 ± 0.05 and 0.09 ± 0.01 respectively. The F^+/U^+ ratio for the samples stored in low relative humidity air showed no decrease compared to the freshly-prepared samples, indicating that little or no ageing had occurred after 7 weeks of storage under these conditions. In addition, single-factor ANOVA analysis ($\alpha = 0.05$) concluded that the F^+/U^+ variance associated with the different temperature and lighting conditions in these dry air samples did not exceed the variance expected from random error.

Even though the particle samples showed significant within-sample-variability, the intensity of the fluorine ions and the resulting F^+/U^+ ratios were up to one order of magnitude lower for the samples stored in high humidity conditions (7-8), compared to those kept in a dry atmosphere (3-6).

Using CLIFS, we analyzed five sapphire specimens with uranium oxyfluoride particles that had been stored in the dark under an argon or nitrogen atmosphere since their preparation at the IRMM. These showed similar spectral features in terms of the number, wavelength, and relative intensities of the peaks. However, the overall intensity of the spectra varied from one sample to the next, most likely as a result of different numbers of particles on the substrates. A representative spectrum (B7SAF23) is shown in Figure 4, along with reference spectra for several different types of U(VI) compounds collected previously. These compounds include a calcium hydroxyuranate

(becquerelite), a hydrated and a dehydrated uranyl oxide (schoepite), a potassium hydroxyuranate (compregnacite), a uranyl silicate (boltwoodite), a uranyl carbonate (liebigite), and a uranyl phosphate (meta-autunite).
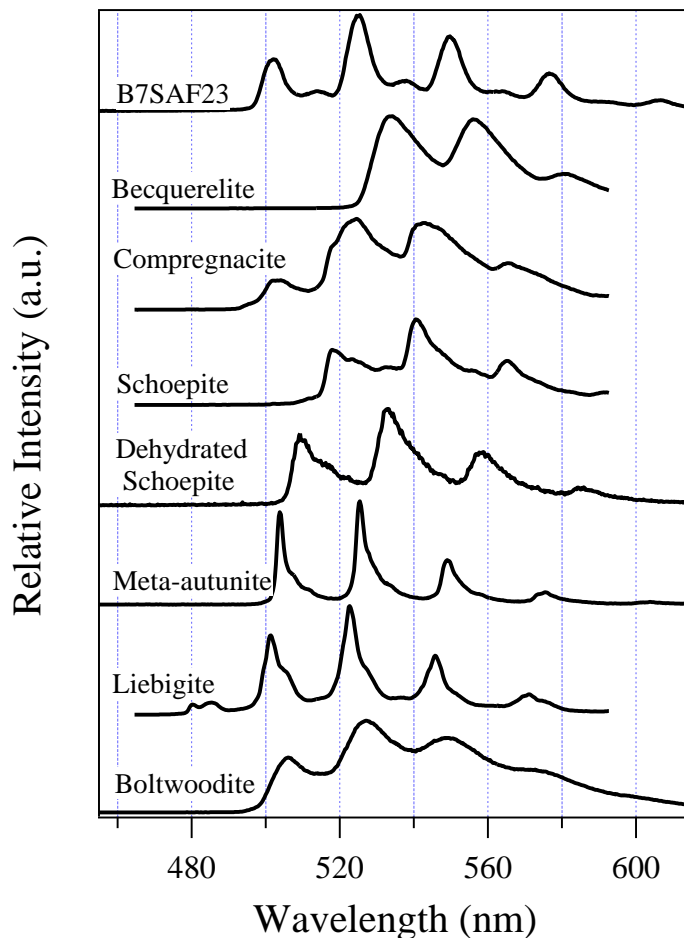
Fig. 4. CLIFS spectra for UO_2F_2 particles stored in the dark under Ar/N_2 before analysis (B7SAF23) and for seven reference minerals containing U(VI).

The B7SAF23 spectrum showed two sets of peaks with similar spacings and relative intensities indicating that two species might be present. The first set of peaks (502, 523, 535, and 578 nm) is much more intense than the second set (515, 539, 564, and 590 nm), and is located at wavelengths similar to those for meta-autunite and liebigite. This set of peaks corresponds well with other reported spectra for UO_2F_2 [8]. The second set of peaks is similar in wavelength, but slightly blue-shifted, to those seen for schoepite. Our tentative interpretation is that the second set of peaks represents particles that have one or more waters of hydration, and we expect the intensities of these peaks to increase with further aging of the particles under humid conditions. It is also possible that the second set of peaks are for a schoepite-like compound that does not contain any fluoride.

CONCLUSION

In this study, the Cameca NanoSIMS 50 was successfully applied to the analysis of individual UO_2F_2 particles, prepared from the hydrolysis of UF_6. Reproducible depth profiles were recorded on ion species ranging from C^+ to UO_2^+. To investigate the rate of fluorine loss, the relative amount of fluorine was measured shortly after preparation and after 7 weeks of storage in various humidity, temperature and lighting conditions. The high spatial resolution NanoSIMS allowed for the analysis of individual particles and detected a significant decrease in the relative amount of fluorine for particles stored in high humidity conditions. For the particles stored in dry air at both 40 °C and 25 °C, and in different lighting conditions, no significant decrease in the relative amount of fluorine could be detected.

CLIFS spectra for the UO_2F_2 samples that had not been exposed to light or humidity were distinct from those of other uranyl solids. The spectra contained two sets of peaks, suggesting that two species, tentatively identified as UO_2F_2 and a small amount of a hydrated UO_2F_2 or UO_2 moiety, were present in these samples.

The various samples will continue to be monitored, and the next analyses are planned after 15 weeks of storage. This series of measurements will provide us with better insights on the aging of UO_2F_2 particles and will allow us to determine the environmental parameters that accelerate the process.

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